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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

This invention Safeties, such as prevention from overcharge of a cell, and a cycle characteristic, electric capacity, It is related with the new lithium secondary battery which can provide the lithium secondary battery excellent also in battery characteristics, such as a conservation characteristic, and the method of securing the safety of the lithium secondary battery, and the electrolysis solution for lithium secondary batteries whose safety is still higher.

[0002]

[Description of the Prior Art]

In recent years, the lithium secondary battery is widely used as power supplies for a drive, such as sized electronic equipment. Not only a portable electron and communication equipment, such as a small video camera, a cellular phone, and a notebook sized personal computer, but the expectation as a power supply for cars is great. This lithium secondary battery mainly comprises an anode, nonaqueous electrolyte, and a negative electrode.

In particular, lithium multiple oxides, such as LiCoO_2 , are used as an anode, and the lithium secondary battery which used the carbon material or the lithium metal as the negative electrode is used suitably. And as a nonaqueous solvent of the electrolysis solution for lithium secondary batteries, carbonate, such as ethylene carbonate (EC) and propylene carbonate (PC), is used suitably.

[0003]

In a negative electrode, a deposit of superfluous lithium arises and a dendrite produces such a lithium secondary battery at the same time lithium superfluous from an anode at the time of overcharge which exceeds the usual operation voltage is emitted. Therefore, the two poles of right and a negative electrode destabilize chemically. If the two poles of right and a negative electrode become unstable chemically, it will act with the carbonate in nonaqueous electrolyte soon, and will decompose, and a rapid exoergic reaction will occur. By this, a cell generates heat unusually and produces the problem that the safety of a cell is spoiled. Such a situation poses such an important problem that the energy density of a lithium secondary battery increases.

[0004]

In order to solve such a problem, the thing which enabled it to secure safety to a surcharge was proposed in

JP,7-302614,A, for example by adding a little aromatic compounds as an additive agent in an electrolysis solution. In this JP,7-302614,A, the anisole derivative with a pi electron orbit which has a reversibility oxidation-reduction potential in electropositive potential rather than the anode potential at the time of a full charge with 500 or less molecular weight, etc. are used as an additive agent of an electrolysis solution. Such an anisole derivative has secured the safety of a cell to a surcharge by carrying out a redox shuttle within a cell.

[0005]

In JP,9-106835,A, use a carbon material for a negative electrode and as an additive agent of an electrolysis solution, When biphenyl, a 3-R-thiophene, 3-chlorothiophene, and a franc are used about 1 to 4% and biphenyl etc. polymerize on the voltage exceeding the maximum working voltage of a cell, internal resistance of a cell is enlarged and the method of securing the safety of a cell to a surcharge is proposed. In JP,9-171840,A, biphenyl, a 3-R-thiophene, 3-chlorothiophene, and a franc are used similarly, When biphenyl etc. polymerize on the voltage exceeding the maximum working voltage of a cell, by generating a gas and operating an internal electroscission device, an internal short circuit is produced and the method of securing the safety of a cell to a surcharge is proposed. In JP,10-321258,A. When similarly biphenyl, a 3-R-thiophene, 3-chlorothiophene, and a franc are used and biphenyl etc. polymerize on the voltage exceeding the maximum working voltage of a cell, By generating a conductive polymer, the method of producing an internal short circuit and securing the safety of a cell to a surcharge is proposed.

[0006]

However, in JP,11-162512,A. In the state of the charge and discharge by which a cycle is repeated to the voltage maximum exceeding 4.1V in the cell which added biphenyl etc., or protracted exposure is carried out at a not less than 40 ** elevated temperature, It is indicated that there is a tendency to worsen battery characteristics, such as a cycle characteristic, and there is a problem that the tendency becomes remarkable, with increase of an addition. Then, when the electrolysis solution which adds 2,2-diphenylpropane etc. is proposed and 2,2-diphenylpropane etc. polymerize on the voltage exceeding the maximum working voltage of a cell, By generating a gas, operating an internal electroscission device or generating a conductive polymer, an internal short circuit is produced and the method of securing the safety of a cell to a surcharge is proposed.

[0007]

[Problem(s) to be Solved by the Invention]

However, the anisole derivative proposed by JP,7-302614,A produced the problem of having an adverse effect on a cycle characteristic or a conservation characteristic, to acting effectively to a surcharge by a redox shuttle. If exposed to local somewhat high voltage, an anisole derivative will decompose gradually with charge and discharge, and the anisole derivative proposed has the problem that an original battery characteristic falls, when usually using it with operating potential, a not less than 40 ** elevated temperature and. Therefore, since an anisole derivative decomposes and decreases gradually with the usual charge and discharge, if a overcharge examination is done after 300 cycles, safety may be unable to be ensured enough.

[0008]

JP,9-106835,A, JP,9-171840,A, As opposed to acting on the biphenyl proposed by JP,10-321258,A, a 3-R-thiophene, 3-chlorothiophene, and Mr. franc **** effectively to a surcharge, It had the adverse effect on the

cycle characteristic or the conservation characteristic, and the problem of becoming remarkable with a biphenyl addition was produced as pointed out by aforementioned JP,11-162512,A. Since oxidative degradation of the biphenyl etc. is carried out this with the potential not more than 4.5V, if it is exposed to a not less than 40 ** elevated temperature or voltage local somewhat high also when usually using it with operating potential, since biphenyl etc. decompose and decrease gradually, a cycle life will fall. Since biphenyl etc. decompose and decrease gradually with charge and discharge, if a overcharge examination is done after 300 cycles, safety may be unable to be ensured enough.

[0009]

Although the safety to a surcharge is not so good as the cell by which the cell which added the 2,2-diphenylpropane proposed by JP,11-162512,A added biphenyl, the safety to a surcharge is better than the cell which nothing adds. It is indicated rather than the cell which nothing adds although the cycle characteristic superior to the cell by which the cell which added 2,2-diphenylpropane added biphenyl is acquired that a cycle characteristic is bad. Therefore, in order to acquire a cycle characteristic better than the cell which added biphenyl, it is said that sacrificing a part of safety can approve.

Thus, as a mechanism of the conventional prevention from overcharge, By polymerizing in the method and the potential not more than 4.5V which carry out a redox shuttle with the potential of the 4.5V neighborhood, Although an internal short circuit is produced by producing an internal short circuit by generating the method and gas which enlarge internal resistance of a cell, and operating an internal electroscission device, or generating a conductive polymer and the method of securing the safety of the cell to a surcharge is known, The actual condition is that battery characteristics, such as safeties, such as prevention from overcharge, and a cycle characteristic, electric capacity, and a conservation characteristic, are not necessarily satisfactory.

[0010]

This invention solves SUBJECT about the above electrolysis solutions for lithium secondary batteries, The lithium secondary battery which can constitute the lithium secondary battery excellent also in battery characteristics, such as safeties, such as prevention from overcharge of a cell, and a cycle characteristic, electric capacity, and a conservation characteristic, And it aims at providing the method of securing the safety of the lithium secondary battery, and the electrolysis solution for lithium secondary batteries whose safety is still higher.

[0011]

[Means for Solving the Problem]

An anode which consists of a multiple oxide with lithium in which this invention contains cobalt or nickel, In a lithium secondary battery which consists of a negative electrode which consists of material which emits [occlusion and] a lithium metal, a lithium alloy, or lithium, and nonaqueous electrolyte by which an electrolyte is dissolved in a nonaqueous solvent, Into this nonaqueous electrolyte, make an organic compound contain and this organic compound decomposes at the time of overcharge, It is related with a lithium secondary battery securing the safety of a cell, its electrolysis solution for lithium secondary batteries, and a method of securing the safety of a cell by coating an activity lithium metal which deposited on a negative electrode (inactivation).

[0012]

Unlike the conventional example, said organic compound contained in nonaqueous electrolyte a mechanism

of prevention from overcharge of this invention by carrying out oxidative degradation electrochemically with potential of +4.6V - +5.2V to lithium, A reaction of an activity lithium metal which deposited on a negative electrode at the time of overcharge, and carbonate in nonaqueous electrolyte is inhibited beforehand, an activity lithium metal which deposited on a negative electrode is coated (inactivation), and it is thought that a overcharge preventive effect is revealed. As a result, the safety of a cell is presumed to be what is secured enough.

[0013]

Since said organic compound contained in nonaqueous electrolyte has oxidation potential as high as +4.6V - +5.2V to lithium, even if it usually repeats charge and discharge with operating potential, in voltage, said organic solvent does not decompose [a not less than 40 ** elevated temperature or] exceeding 4.2V locally. It is thought that it not only excels in safeties, such as prevention from overcharge of a cell, but it can provide a lithium secondary battery excellent also in battery characteristics, such as a cycle characteristic, electric capacity, and a conservation characteristic, by this.

[0014]

[Embodiment of the Invention]

The following compounds are mentioned as said organic compound contained in the electrolysis solution by which the electrolyte is dissolved in the nonaqueous solvent. The oxidation potential to the lithium measured by the method indicated in the example which carries out a postscript is shown in a parenthesis.

As said organic compound, a ketone compound is used suitably [at least one sort], 3-methyl-2-butanone (4.9V), 2-methyl-3-pentanone (4.9V), 2,4-dimethyl- 3-pentanone (5.2V), 3-methyl-2-pentanone (4.9V), 4-methyl-3-hexanone (4.9V), 3,5-dimethyl- 4-heptanone (5.1V), 3,3-dimethyl- 2-pentanone (5.1V), pinacolin (5.1V), 2,2-dimethyl- 3-pentanone (5.1V), 2,2,4-trimethyl 3-pentanone (5.0V), 2,2,4,4-tetramethyl 3-pentanone (4.9V), 3,4-dimethyl- 2-pentanone (4.9V), 3,5-dimethyl- 2-hexanone (4.9V), 3,4-dimethyl- 2-hexanone (4.9V), 3-isopropyl-2-heptanone (4.9V), 2,4-dimethyl cyclobutanone (5.0V), 2,2,4,4-tetramethyl cyclobutanone (4.9V), 2,5-dimethylcyclopentanone (5.0V), 2,2,5,5-tetramethyl cyclopentanone (4.9V), (-)-CHUJON (4.9V), 2,6-dimethylcyclohexanone (5.0V), 2,2,6,6-tetramethyl cyclohexanone (4.9V), 2,6-di-tert-butylcyclohexanone (4.9V), 2,6-di-sec-butylcyclohexanone (4.9V), 2-sec-butylcyclohexanone (4.9V), (-)-menthone (4.8V), (+)-menthone (4.8V), (**)-menthone (4.8V), isomenthone (4.8V), (-)-camphor (5.0V), (+)-camphor (5.0V), (**)-camphor (5.0V), (+)-NOPINON (4.9V), 2,7-dimethyl cycloheptanone (4.9V), (-)-fenchone (4.6V), (+)-fenchone (4.6V), (**)-fenchone (4.6V), 2-ADAMANTANON (5.2V), etc. may be mentioned, and these may be used by one kind, and it may be used combining two or more kinds. However, this invention is not limited to these compounds.

[0015]

Cyclohexylbenzene (4.7V) can be used together as said organic compound, and when oxidation potential adds the cyclohexylbenzene which is 4.7V to said ketone compound especially whose oxidation potential is 4.6-5.2V, a overcharge preventive effect can be raised. When adding cyclohexylbenzene, for example to fenchone, as for the content of fenchone, 4 times the amount or less is preferred to the weight of cyclohexylbenzene, and its 0.5-2.5 times the amount is especially preferably preferred in 0.3-3 times the amount. A overcharge preventive effect can be heightened by using together said at least two kinds from which oxidation potential differs as described above of organic compounds. However, by carrying out oxidative degradation with the potential of +4.6V - +5.0V to lithium, The reaction of the activity lithium metal

which deposited on the negative electrode at the time of overcharge, and carbonate in nonaqueous electrolyte is inhibited beforehand, and if it is an organic compound in which coating (inactivation) of the activity lithium metal which deposited on the negative electrode is promoted, this invention will not be limited to these compounds at all. As a compound which has the same effect as said cyclohexylbenzene, 1-fluoro-2-cyclohexylbenzene (4.8V), 1-fluoro-3-cyclohexylbenzene (4.8V), 1-fluoro-4-cyclohexylbenzene (4.8V), 1-chloro-4-cyclohexylbenzene (4.8V), The cyclohexylbenzene compound of halogen atom substitution, such as 1-bromo-4-cyclohexylbenzene (4.8V) and 1-iodo-4-cyclohexylbenzene (4.8V), can be mentioned suitably.

[0016]

Similarly, as said organic compound, by using together at least one sort of a tert-alkylbenzene compound, since a overcharge preventive effect can be raised further, it is desirable. For example, tert-butylbenzene (4.9V), 1-fluoro-4-tert-butylbenzene (4.9V), 1-chloro-4-tert-butylbenzene (4.9V), 1-bromo-4-tert-butylbenzene (4.9V), 1-iodo-4-tert-butylbenzene (4.9V), 5-tert-butyl-m-xylene (4.6V), 4-tert-butyltoluene (4.7V), 3,5-di-tert-butyltoluene (4.8V), 1,3-di-tert-butylbenzene (4.9V), 1,4-di-tert-butylbenzene (4.9V), The tert-butylbenzene compound replaced by the straight chain or branching alkyl group of halogen atoms, such as 1,3,5-tri-tert-butylbenzene (5.0V), or the carbon numbers 1-12 is mentioned, tert-pentylbenzene (4.8V), 1-fluoro-4-tert-pentylbenzene (4.8V), 1-chloro-4-tert-pentylbenzene (4.8V), 1-bromo-4-tert-pentylbenzene (4.8V), 1-iodo-4-tert-pentylbenzene (4.8V), 1-methyl-4-tert-pentylbenzene, (4.7V) 5-tert-pentyl-m-xylene (4.6V), 1-ethyl-1-(methylpropyl) benzene (4.8V), benzene (1,1-diethylpropyl) (4.8V), The tert-alkylbenzene compound replaced by the straight chain or branching alkyl group of halogen atoms, such as 1,3-di-tert-pentylbenzene (4.7V) and 1,4-di-tert-pentylbenzene (4.7V), or the carbon numbers 1-12 is mentioned.

[0017]

Both a cyclohexylbenzene compound and a tert-alkylbenzene compound can also be used together to a ketone compound. For example, one or more sorts chosen from cyclohexylbenzene and tert-butylbenzene, tert-pentylbenzene, 1-fluoro-4-tert-butylbenzene, and 1-fluoro-4-tert-pentylbenzene are mentioned to a ketone compound like fenchone.

[0018]

In said organic compound, the content of said organic compound, since sufficient overcharge effect will not be acquired if too small [when too large, the electric conductivity of an electrolysis solution, etc. may change and battery capacity may fall, and], 1 to 5% of the weight of the range is especially preferred to the weight of an electrolysis solution 0.1 % of the weight - 10% of the weight.

[0019]

As a nonaqueous solvent used by this invention, for example Ethylene carbonate (EC), Propylene carbonate (PC), butylene carbonate (BC), Cyclic carbonate, such as vinylene carbonate (VC), and lactone, such as gamma-butyrolactone. Annular sulfonic acid, such as a 1,3-propane sultone, dimethyl carbonate (DMC), Chain carbonate, such as methylethyl carbonate (MEC) and diethyl carbonate (DEC). A tetrahydrofuran, 2-methyltetrahydrofuran, 1,4-dioxane, Amide, such as ester species, such as nitril, such as ether, such as 1,2-dimethoxyethane, 1,2-diethoxyethane, and 1,2-dibutoxyethane, and acetonitrile, methyl propionate, methyl pivalate, and octyl pivalate, and dimethylformamide, is mentioned.

[0020]

These nonaqueous solvents may be used by one kind, and may be used combining two or more kinds.

Although the combination in particular of a nonaqueous solvent is not limited, various combination, such as combination of cyclic carbonate and chain carbonate, combination of cyclic carbonate and lactone, and combination of three kinds of cyclic carbonate and chain carbonate, is mentioned, for example.

[0021]

As an electrolyte used by this invention, for example LiPF_6 , LiBF_4 , LiClO_4 , $\text{LiN}(\text{SO}_2\text{CF}_3)_2$, $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$, $\text{LiC}(\text{SO}_2\text{CF}_3)_3$, $\text{LiPF}_4(\text{CF}_3)_2$, $\text{LiPF}_3(\text{C}_2\text{F}_5)_3$, $\text{LiPF}_3(\text{CF}_3)_3$, $\text{LiPF}_3(\text{iso-C}_3\text{F}_7)_3$, $\text{LiPF}_5(\text{iso-C}_3\text{F}_7)$, etc. are mentioned. These electrolytes may be used by one kind, and they may be used, combining them two or more kinds. 0.1-3 M of these electrolytes are usually preferably dissolved and used for the aforementioned nonaqueous solvent by the concentration of 0.5-1.5M.

[0022]

The electrolysis solution of this invention is obtained by mixing the aforementioned nonaqueous solvent, dissolving the aforementioned electrolyte in this for example, and dissolving at least one sort in said organic compound.

[0023]

The electrolysis solution of this invention is suitably used as the members forming of a rechargeable battery, especially members forming of a lithium secondary battery. Especially about members forming other than the electrolysis solution which constitutes a rechargeable battery, it is not limited but various members forming currently used conventionally can be used.

[0024]

For example, a composite metal oxide with the lithium which contains cobalt or nickel as positive active material is used. As such a composite metal oxide, LiCoO_2 , LiNiO_2 , $\text{LiCo}_{1-x}\text{nickel}_x\text{O}_2$ ($0.01 < x < 1$), etc. are mentioned, for example. It may be used like LiCoO_2 , LiMn_2O_4 and LiCoO_2 , LiNiO_2 , and LiMn_2O_4 and LiNiO_2 , mixing suitably.

[0025]

An anode the aforementioned positive active material A conducting agent and polytetrafluoroethylenes (PTFE), such as acetylene black and carbon black, Polyvinylidene fluoride (PVDF), the copolymer (SBR) of styrene and butadiene, After kneading with acrylonitrile and binders, such as a copolymer (NBR) of butadiene, and carboxymethyl cellulose (CMC), and considering it as positive electrode mixture, This positive electrode material is rolled to the foil and the Russ board of aluminum as a charge collector, or the product made from stainless steel, and it is produced by heat-treating under a vacuum at the temperature of 50 ** - about 250 ** for about 2 hours.

[0026]

The carbon material as a negative electrode (negative electrode active material) which can emit [occlusion and] a lithium metal, a lithium alloy, or lithium [Pyrolytic carbon, corks, graphite, an organic polymer compound (artificial-graphite, natural graphite, etc.) combustion body, carbon fiber] Or substances, such as a compound tin oxidation thing, are used. It is preferred that the spacing (d_{002}) of a lattice plane (002) uses especially the carbon material which has a graphite mold crystal structure which is 0.335-0.340 nm (nano meter). Powder material like a carbon material An ethylene propylene diene terpolymer (EPDM), Polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), It kneads with binders, such as a copolymer

(SBR) of styrene and butadiene, a copolymer (NBR) of acrylonitrile and butadiene, and carboxymethyl cellulose (CMC), and is used as negative electrode mixture.

[0027]

The structure in particular of a lithium secondary battery is not limited, and a cylindrical cell, a square-shaped cell, etc. which have the anode of a monolayer or a double layer, a negative electrode, the coin type cell which has a separator and a polymer battery, an anode of further rolled form, a negative electrode, and a rolled form separator are mentioned as an example. The fine porous membrane of polyolefine publicly known as a separator, textile fabrics, a nonwoven fabric, etc. are used.

[0028]

The lithium secondary battery in this invention has the outstanding cycle characteristic over the long period of time, also when maximum working voltage is larger than 4.2V, and it has the cycle characteristic which was excellent also when especially maximum working voltage was 4.3V. Cut-off voltage can be made more than 2.0V, and also can be made more than 2.5V. Although not limited in particular for a current value, it is usually used by the constant current discharge of 0.1 - 3C. Although the charge and discharge of the lithium secondary battery in this invention can be carried out to -40-100 ** in the wide range, it is 0-80 ** preferably.

[0029]

[Example]

Next, an example and a comparative example are given and this invention is explained concretely.

Example 1

[Measurement of oxidation potential]

After having dissolved LiPF_6 in the nonaqueous solvent of propylene carbonate so that it might become the concentration of 1M, and adjusting an electrolysis solution, it added so that it might become 3 % of the weight to an electrolysis solution at this about (+)-fenchone as said organic compound. Oxidation potential was measured at the room temperature (20 **) using the electrochemistry analyzer by ALS (model 608A). Metal lithium foil was used for the reference electrode, and the platinum pin electrode (1 mm in diameter) was used for the working pole. It swept from +3V to +6V at the speed of 10 mV/s. It was specified as oxidation potential with the value of potential when a 0.1-mA current change is accepted. However, the 2nd place of the decimal point rounded off. As a result, the oxidation potential of (+)-fenchone was 4.6V.

[0030]

[Preparation of an electrolysis solution]

After having prepared the nonaqueous solvent of EC/DEC(capacity factor) =30/70, having dissolved so that it might become the concentration of 1M about LiPF_6 at this, and preparing an electrolysis solution, (+)-fenchone was further added as said organic compound so that it might become 3 % of the weight to an electrolysis solution.

[0031]

[Production of a lithium secondary battery, and measurement of a battery characteristic]

Acetylene black (conducting agent) was mixed 5% of the weight 90% of the weight, polyvinylidene fluoride (binder) was mixed for LiCoO_2 (positive active material) at 5% of the weight of a rate, the 1-methyl-2-pyrrolidone was added to this, and it was made slurry form, and applied on aluminum foil. Then, pressing of this was dried and carried out and the anode was prepared. The artificial graphite (negative electrode active

material) was mixed 95% of the weight, polyvinylidene fluoride (binder) was mixed at 5% of the weight of a rate, the 1-methyl-2-pyrrolidone was added to this, and it was made slurry form, and applied on copper foil. Then, pressing of this was dried and carried out and the negative electrode was prepared. And using the separator of a polypropylene fine porous film, the above-mentioned electrolysis solution was poured in and the cylindrical cell (18 mm in diameter and 65 mm in height) of 18650 sizes was produced. The pressure release mouth and the internal current cutoff device were formed in the cell.

In order to do a cycle test using these 18650 cells, after charging to 4.2V by the constant current of 1.45A (1C), it charged under the constant voltage as the final voltage 4.2V under the elevated temperature (45 **) for a total of 3 hours. Next, under the constant current of 1.45A (1C), it discharged to the final voltage 2.5V, and charge and discharge were repeated. Initial service capacity was equivalent as compared with the case (comparative example 1) where 1M LiPF₆+EC/DEC(capacity factor) =30/70 are used as an electrolysis solution. When the battery characteristic after 300 cycles was measured, and initial service capacity was made into 100%, the service capacity maintenance factor was 86.1%. The high temperature conservation characteristic was also good. The overcharge examination was done under ordinary temperature (20 **) using 18650 cells which repeated the cycle test 300 times by charging continuously by the constant current of 2.9A (2C) from a full charge state. At this time, the maximum surface temperature of the cell after current cutoff was 78 ** current cutoff time for 24 minutes. The material conditions and the battery characteristic of a cylindrical cell of 18650 sizes are shown in Table 1.

[0032]

Example 2

As said organic compound, (+)-fenchone was used 5% of the weight to the electrolysis solution, and also oxidation potential was measured like Example 1. A result is shown in Table 1. The maximum surface temperature of the cell after the material conditions of the cylindrical cell of 18650 sizes and the service capacity maintenance factor after 300 cycles, current cutoff time, and current cutoff is shown in Table 1.

[0033]

Comparative example 1

It did not add at all and also said organic compound measured oxidation potential like Example 1. A result is shown in Table 1. The maximum surface temperature of the cell after the material conditions of the cylindrical cell of 18650 sizes and the service capacity maintenance factor after 300 cycles, current cutoff time, and current cutoff is shown in Table 1.

[0034]

Example 3

As said organic compound, (+)-fenchone and 1-fluoro-4-tert-pentylbenzene were used 1.5% of the weight 3% of the weight to the electrolysis solution, respectively, and also oxidation potential was measured like Example 1. A result is shown in Table 1. The maximum surface temperature of the cell after the material conditions of the cylindrical cell of 18650 sizes and the service capacity maintenance factor after 300 cycles, current cutoff time, and current cutoff is shown in Table 1. Compared with Example 1, the temperature after current cutoff is low, and current cutoff time is also short, and it turns out that it excels in the overcharge preventive effect further compared with Example 1.

[0035]

Example 4

As said organic compound, (+)-fenchone and tert-pentylbenzene were used 2% of the weight 3% of the weight to the electrolysis solution, respectively, and also oxidation potential was measured like Example 1. A result is shown in Table 1. The maximum surface temperature of the cell after the material conditions of the cylindrical cell of 18650 sizes and the service capacity maintenance factor after 300 cycles, current cutoff time, and current cutoff is shown in Table 1. Compared with Example 1, the temperature after current cutoff is low, and current cutoff time is also short, and it turns out that it excels in the overcharge preventive effect further compared with Example 1.

[0036]

Example 5

As said organic compound, (-)-fenchone and tert-pentylbenzene were used 2% of the weight 3% of the weight to the electrolysis solution, respectively, and also oxidation potential was measured like Example 1. A result is shown in Table 1. The maximum surface temperature of the cell after the material conditions of the cylindrical cell of 18650 sizes and the service capacity maintenance factor after 300 cycles, current cutoff time, and current cutoff is shown in Table 1. Compared with Example 1, the temperature after current cutoff is low, and current cutoff time is also short, and it turns out that it excels in the overcharge preventive effect further compared with Example 1.

[0037]

Example 6

As said organic compound, (+)-fenchone and cyclohexylbenzene were used 1% of the weight 3% of the weight to the electrolysis solution, respectively, and also oxidation potential was measured like Example 1. A result is shown in Table 1. The maximum surface temperature of the cell after the material conditions of the cylindrical cell of 18650 sizes and the service capacity maintenance factor after 300 cycles, current cutoff time, and current cutoff is shown in Table 1. Compared with Example 1, the temperature after current cutoff is low, and current cutoff time is also short, and it turns out that it excels in the overcharge preventive effect further compared with Example 1.

[0038]

Comparative examples 2-4

As said organic compound, publicly known 4-fluoroanisole (comparative example 2), 2-chlorothiophene (comparative example 3), and biphenyl (comparative example 4) were added 2% of the weight to the electrolysis solution, respectively, and also oxidation potential was measured like Example 1. A result is shown in Table 1. The maximum surface temperature of the cell after the material conditions of the cylindrical cell of 18650 sizes and the service capacity maintenance factor after 300 cycles, current cutoff time, and current cutoff is shown in Table 1.

[0039]

Example 7

As positive active material, replace with LiCoO_2 and $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ is used, (+)-fenchone and tert-pentylbenzene were used 1% of the weight 3% of the weight to the electrolysis solution, respectively as said organic compound, and also the cylindrical cell of 18650 sizes was produced like Example 1, and battery capacity was measured. The material conditions and the battery characteristic of a cylindrical cell of 18650 sizes are shown in Table 1.

[0040]

Comparative example 5

As positive active material, replaced with LiCoO_2 , and $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ was used, and also the cylindrical cell of 18650 sizes was produced like the comparative example 1, and battery capacity was measured. The material conditions and the battery characteristic of a cylindrical cell of 18650 sizes are shown in Table 1.

[0041]

Example 8

The nonaqueous solvent of EC/VC/DEC(capacity factor) =30/2/68 is prepared, After dissolving LiPF_6 in this so that it may become the concentration of 1M, and preparing an electrolysis solution, Furthermore, (+)-fenchone, tert-pentylbenzene, and cyclohexylbenzene were used 1% of the weight 2% of the weight 3% of the weight to the electrolysis solution, respectively as an organic compound, and also the cylindrical cell of 18650 sizes was produced like Example 1, and battery capacity was measured. The material conditions and the battery characteristic of a cylindrical cell of 18650 sizes are shown in Table 2. Compared with Example 1, the temperature after current cutoff is low, and current cutoff time is also short, and it turns out that it excels in the overcharge preventive effect further compared with Example 1.

[0042]

Example 9

As said organic compound, (+)-fenchone, tert-butylbenzene, and cyclohexylbenzene were used 1% of the weight 2% of the weight 3% of the weight to the electrolysis solution, respectively, and also the cylindrical cell of 18650 sizes was produced like Example 8, and battery capacity was measured. The material conditions and the battery characteristic of a cylindrical cell of 18650 sizes are shown in Table 2. Compared with Example 1, the temperature after current cutoff is low, and current cutoff time is also short, and it turns out that it excels in the overcharge preventive effect further compared with Example 1.

[0043]

Example 10

As said organic compound, (+)-fenchone, tert-pentylbenzene, and tert-butylbenzene were used 1% of the weight 1% of the weight 4% of the weight to the electrolysis solution, respectively, and also the cylindrical cell of 18650 sizes was produced like Example 8, and battery capacity was measured. The material conditions and the battery characteristic of a cylindrical cell of 18650 sizes are shown in Table 2.

[0044]

Example 11

As said organic compound, (+)-fenchone and 1-fluoro-4-cyclohexylbenzene were used 1% of the weight 4% of the weight to the electrolysis solution, respectively, and also the cylindrical cell of 18650 sizes was produced like Example 8, and battery capacity was measured. The material conditions and the battery characteristic of a cylindrical cell of 18650 sizes are shown in Table 2.

[0045]

Comparative example 6

The nonaqueous solvent of EC/VC/DEC(capacity factor) =30/2/68 was used, and also the cylindrical cell of 18650 sizes was produced like the comparative example 1, and battery capacity was measured. The material conditions and the battery characteristic of a cylindrical cell of 18650 sizes are shown in Table 2.

[0046]

As for the above example, cobalt or nickel sufficient on a negative electrode all deposited at the time of overcharge. The cell which added the organic compound of this invention is understood that the safety and cycle characteristic over a surcharge are better than the cell of a comparative example.

[0047]

[Table 1]

	正極	負極	有機化合物 :量(wt%)	酸化 電位 (V)	電解液組成 容量比	電流遮 断時間 (分)	電池の 最高温 度(°C)	300 サイクル 放電容 量維持 率%
実施 例1	LiCoO ₂	人造 黒鉛	(+)ーフェンコン :3	4.6	1M LiPF ₆ EC/DEC =30/70	24	78	86.1
実施 例2	LiCoO ₂	人造 黒鉛	(+)ーフェンコン :5	4.6	1M LiPF ₆ EC/DEC =30/70	22	74	85.8
比較 例1	LiCoO ₂	人造 黒鉛	なし	5.4	1M LiPF ₆ EC/DEC =30/70	31	熱暴走	82.8
実施 例3	LiCoO ₂	人造 黒鉛	(+)ーフェンコン :3 1-フルオロ-4-tert-ペンチ ルベンゼン :1.5	4.6 + 4.8	1M LiPF ₆ EC/DEC =30/70	20	71	85.7
実施 例4	LiCoO ₂	人造 黒鉛	(+)ーフェンコン :3 tert-ペンチルベンゼン :2	4.6 + 4.8	1M LiPF ₆ EC/DEC =30/70	20	70	85.9
実施 例5	LiCoO ₂	人造 黒鉛	(-)ーフェンコン :3 tert-ペンチルベンゼン :2	4.6 + 4.8	1M LiPF ₆ EC/DEC =30/70	20	70	85.9
実施 例6	LiCoO ₂	人造 黒鉛	(+)ーフェンコン :3 シクロヘキシルベンゼン :1	4.6 + 4.7	1M LiPF ₆ EC/DEC =30/70	26	70	85.1
比較 例2	LiCoO ₂	人造 黒鉛	4-フルオロアニソール :2	4.5	1M LiPF ₆ EC/DEC =30/70	22	118	72.6
比較 例3	LiCoO ₂	人造 黒鉛	2-クロロチオフェン:2	4.4	1M LiPF ₆ EC/DEC =30/70	19	92	73.3
比較 例4	LiCoO ₂	人造 黒鉛	ビフェニル:2	4.5	1M LiPF ₆ EC/DEC =30/70	18	83	74.2
実施 例7	LiNi _{0.8} Co _{0.2} O ₂	人造 黒鉛	(+)ーフェンコン :3 tert-ペンチルベンゼン :1	4.6 + 4.8	1M LiPF ₆ EC/DEC =30/70	24	70	85.3
比較 例5	LiNi _{0.8} Co _{0.2} O ₂	人造 黒鉛	なし	5.4	1M LiPF ₆ EC/DEC =30/70	31	熱暴走	80.4

[0048]

[Table 2]

	正極	負極	有機化合物 :量(wt%)	酸化 電位 (V)	電解液組成 容量比	電流遮 断時間 (分)	電池の 最高温 度(°C)	300 サイクル 放電容 量維持 率%
実施 例8	LiCoO ₂	人造 黒鉛	(+)ーフェンコン :3 tert-ペンチルベンゼン :2 シクロヘキシルベンゼン :1	4.6 + 4.8 + 4.7	1M LiPF ₆ EC/VC/DEC =30/2/68	18	65	86.2
実施 例9	LiCoO ₂	人造 黒鉛	(+)ーフェンコン :3 tert-ブチルベンゼン :2 シクロヘキシルベンゼン :1	4.6 + 4.9 + 4.7	1M LiPF ₆ EC/VC/DEC =30/2/68	18	65	86.1
実施 例10	LiCoO ₂	人造 黒鉛	(+)ーフェンコン :4 tert-ペンチルベンゼン :1 tert-ブチルベンゼン :1	4.6 + 4.8 + 4.9	1M LiPF ₆ EC/VC/DEC =30/2/68	22	63	86.9
実施 例11	LiCoO ₂	人造 黒鉛	(+)ーフェンコン :4 1-フルオロ-4-シクロヘキ シルベンゼン :1	4.6 + 4.8	1M LiPF ₆ EC/VC/DEC =30/2/68	19	64	86.5
比較 例6	LiCoO ₂	人造 黒鉛	なし	4.8	1M LiPF ₆ EC/VC/DEC =30/2/68	31	熱暴走	84.3

[0049]

This invention is not limited to the example of a statement, but various combination which can be guessed is easily possible for it from the meaning of an invention. The combination in particular of the solvent of the above-mentioned example is not limited. Although the above-mentioned example is related with the cylindrical cell of 18650 sizes, this invention is applied also to a square shape, an aluminum lamination type, and a coin type cell.

[0050]

[Effect of the Invention]

According to this invention, the lithium secondary battery excellent also in battery characteristics, such as safeties, such as prevention from overcharge of a cell, and a cycle characteristic, electric capacity, and a conservation characteristic, can be provided.

[Translation done.]